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PROCEEDINGS

A MECHANISM FOR BLISTERING OF CARBON FIBER COMPOSITES

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ABSTRACT

Blisters containing fluid with a high pH were induced in a carbon fiber vinyl ester polymer matrix composite by cathodic polarization in a sodium chloride solution. The oxygen content of the solution was varied in order to determine the effect of oxygen on the blister process. It was found that increasing the oxygen content in solution decreased the time for blister initiation, indicating that the reduction of oxygen to form hydroxyl ions was an important reaction. Calculations indicated that a similar cumulative charge density was required for blister initiation for the different oxygen contents, confirming the importance of oxygen to the blister process.

A mechanism for blister formation dependent upon oxygen reduction to hydroxyl ions and the subsequent formation of an osmotic cell is outlined from the results of this study.

INTRODUCTION

Blistering of carbon fiber polymer composites when the fibers are in contact with metals in the presence of sea water or salt water was termed 'galvanic blistering'. Galvanic blistering of carbon reinforced vinyl ester[1], polyester[2], epoxy[3], and polyamide[4] composites were reported. It follows that galvanic blistering is a characteristic degradation generic to several carbon fiber polymer composites. Carbon being electrically conductive and a noble cathodic material, carbon fibers in a carbon fiber polymer composite become cathodes in a galvanic couple formed with metals steel or aluminum. This composite/metal galvanic couple accelerates metal corrosion and therefore, poses a threat to metal structures that are in galvanic contact with carbon fiber composite structures. The galvanic blisters, formed on composite samples, were

filled with liquid with pH up to 14. The blister cavities formed along the fiber/matrix interface[5]. Therefore, growth of galvanic blisters would result in increased fiber/matrix debonding with time. The study of the electrochemical reactions involved and the underlying mechanisms that lead to galvanic blistering of carbon composites will be the focus of this paper.

In the current investigation, galvanic blistering of carbon fiber reinforced vinyl ester composite was studied. The composite samples showed blisters of sizes in the range 1 - 2 mm in diameter and small ones in the range of 10 - 100 μm. The large blisters form in the zones where the polymer thickness is maximum and the small blisters form on the fibers closest to the surface where the polymer thickness is minimum. Figures (1) and (2) show these blisters respectively.
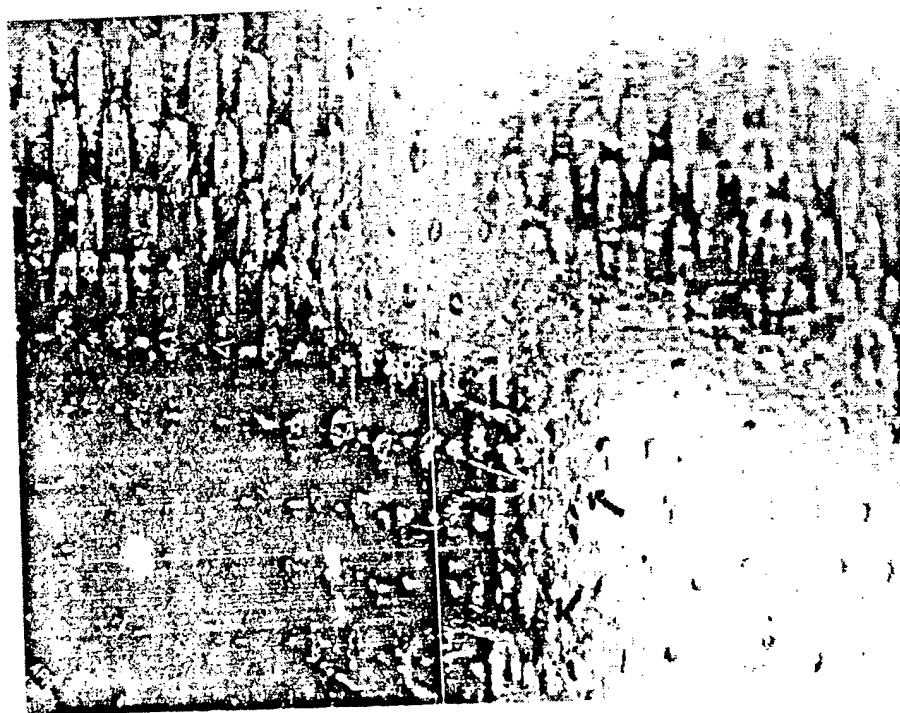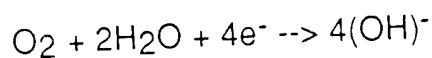

Figure 1. Large galvanic blisters on a carbon fiber vinyl ester composite.

The cathodic reaction on several carbon surfaces in neutral or alkaline environment is the electrocatalytic reduction of dissolved oxygen to hydroxyl ions[6], that in equation form is:

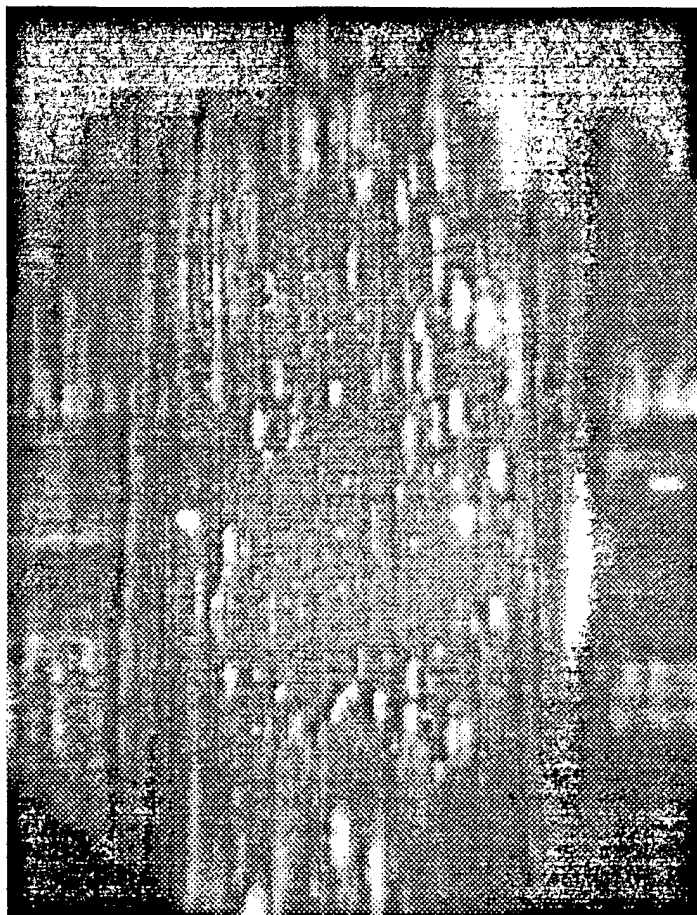$$O_2 + 2H_2O + 4e^- \longrightarrow 4(OH)^-$$

Figure 2. Small galvanic blisters on a carbon fiber vinyl ester composite.

The very high pH of the blister fluids suggests that this reaction is a possibility even on the carbon fibers embedded in a polymer matrix. Therefore, the effects of oxygen concentrations on corrosion currents, galvanic blister formation and electrochemical impedance response was investigated. A mechanism of galvanic blistering is proposed on the assumption that the cathodic reduction of oxygen occurs on carbon fibers in the composite. The results of the oxygen experiments will be discussed in light of the proposed mechanism.

EXPERIMENTAL PROCEDURES

Materials

An orthotropic laminate with unidirectional T300 carbon fiber tapes in a DERAKANE™ 470-36 vinyl ester matrix was studied. The laminate was characterized by a fiber volume fraction of 26%. Samples of dimensions 6 cm x 6 cm x 3 cm were cut from a 3 cm laminate. The resin-

rich faces of the samples were exposed to the electrolyte. The composite has several defects in the form of air bubbles which formed during processing. The exposed area is a 5 cm diameter circular area.

Electrolytes

The basic electrolyte used in the study was a 3.0 weight percent sodium chloride solution. The electrolyte was not changed during the period of experiments. The experiments were conducted at average ambient temperature of 70°F. Three different oxygen partial pressures in the electrolyte were chosen: (a) dissolved oxygen at 1 atmosphere by bubbling pure oxygen gas through the electrolyte; (b) dissolved oxygen at 0.2 atm. from dissolved air at one atmosphere in the electrolyte. (c) dissolved oxygen at 0.06 atm. attained by first preparing degassed sodium chloride solution from a freshly boiled, cooled, de-ionized and distilled water and the subsequent bubbling of nitrogen gas.

The oxygen concentrations were measured using a ORION Model 97-08-00 electrode. Since, the instrument can measure oxygen concentration up to 14 ppm only, the oxygen concentration at higher partial pressures i.e. oxygen concentration at 1 atmosphere was estimated by extrapolation. The activity coefficient was assumed constant in estimating the concentration of oxygen in the solution at a given gaseous partial pressure. Oxygen partial pressures used and the corresponding concentrations are given in the following table:

Oxygen Partial Pressures in gas phase (atmospheres)	Concentrations of O_2 in solution (parts per million by weight)
1.00 (high)	41.25 (estimated)
0.20 (medium)	8.25 (measured)
0.06 (low)	2.25 (measured)

Electrochemical Testing

The electrochemical apparatus for impedance testing is shown in figure (3). The cathodic potential applied to the samples was -0.9 volts versus a saturated calomel electrode (SCE). The potential of -.9 V was chosen because it is below the E_{corr} of carbon with several engineering metals and is the greatest cathodic potential reached above water stability limit. An EG&G PARC model 273 and model 363 potentiostats were employed to apply and maintain the potentials. Current values were recorded at different exposure times. The electrochemical impedance for these samples was also measured at various times during exposure. A Solartron model 1255 HF frequency response analyzer supplied the input signal and analyzed the response signal. The instruments were coordinated and the data acquired using an IBM personal computer. The

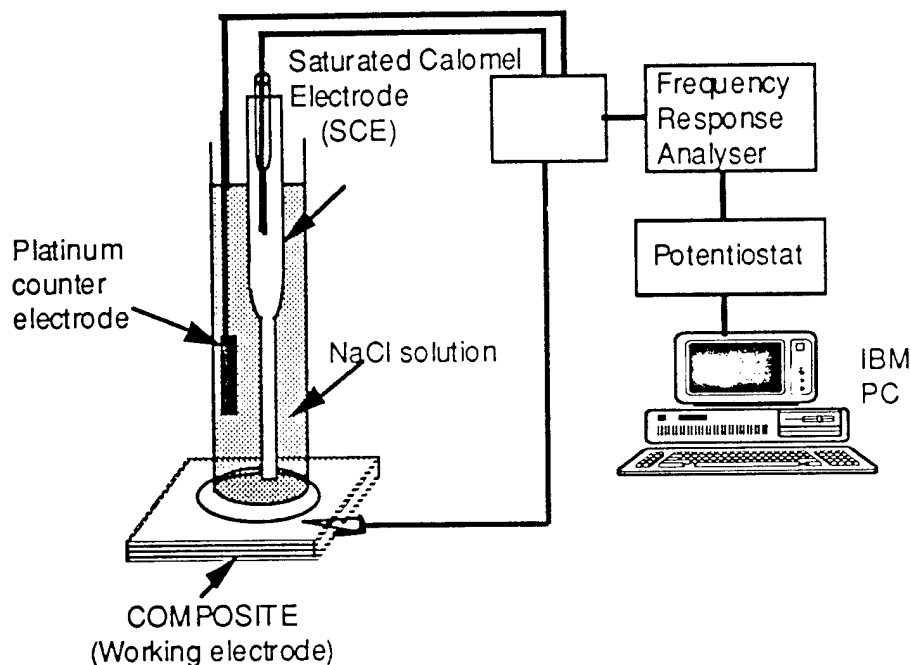EG&G M388 user interactive software was used to execute the experimental procedures.

Figure 3. Experimental apparatus for electrochemical testing.

Surface Examination

Visual examination of samples was also conducted at different times during the period of exposure to examine for blisters. The time for blisters to grow to a diameter approximately 1 mm diameter was arbitrarily termed as the *blister detectability time* (BDT). Only the large blisters were detectable by this technique. The BDT was used as a criterion to compare the rate of blistering of the samples. Therefore, from definition it follows that the lower the BDT, the greater the rate of blister growth and vice-*versa*. The blister detectability times were recorded for the three samples.

RESULTS AND DISCUSSION

The proposed blistering mechanism

From the results of this study a mechanism can be proposed for blister formation. The first part of the process is the initiation of the blister at the carbon fiber/polymer interface. Two possible mechanisms are available to the initiation process. Both of the mechanisms involve the creation of a free volume. The first depends on decreasing the adsorption

of the polymer to the carbon fiber. The carbon fibers develop a negative surface charge when galvanically coupled. As a result, the electron dense parts of the adhering polymer chains do not absorb onto the carbon fibers as strongly. A local aqueous film nucleates in these debonded zones due to the initial zero partial pressure of water in these zones. The movement of water also brings sodium ions and oxygen into the region.

The second mechanism suggests that the carbon fiber to polymer interface is unlikely to be perfect. As a result local areas of no bonding between them will exist. The hydroxyl ion can be formed in these regions as water along with oxygen will tend to permeate to these defect regions preferentially. For both initation mechanisms, oxygen reduction to hydroxyl ions takes place on the carbon surface. As a result sodium hydroxide solution is formed. Sodium hydroxide is highly hygroscopic and draws more water into this region. The coupled effects of (a) relatively greater diffusion rates of water through the polymer compared to sodium hydroxide solution and (b) the rate of production of hydroxyl ions being greater than the hydroxyl ion diffusion away from the cathodic sites, builds an osmotic pressure in the region.

Once the intiation stage is reached, the blister grows due to polymer layer deformation, creep and fiber/matrix interface failure or unzipping under this pressure. The growth is sustained by continuous production of hydroxyl ions which maintains high concentration of sodium hydroxide in the blister liquid. The blister growth therefore results in interface debonding with time.

Oxygen Experimental Results

The measured current densities (current divided by exposure area) as a function of exposure time for the three cases of oxygen concentrations: high, medium and low is shown in figure (4). The current increases to a high value rapidly within a few hours and drops off to a steady value for the cases of high and medium oxygen concentrations.

The steady state current density for the sample exposed to higher oxygen concentration is five times the current density for the case of medium oxygen concentration. At the same time, the high oxygen concentration is five times the medium oxygen concentration. It follows therefore, that the current density of the carbon fibers increases proportionally with increase in oxygen partial pressures in the electrolyte.
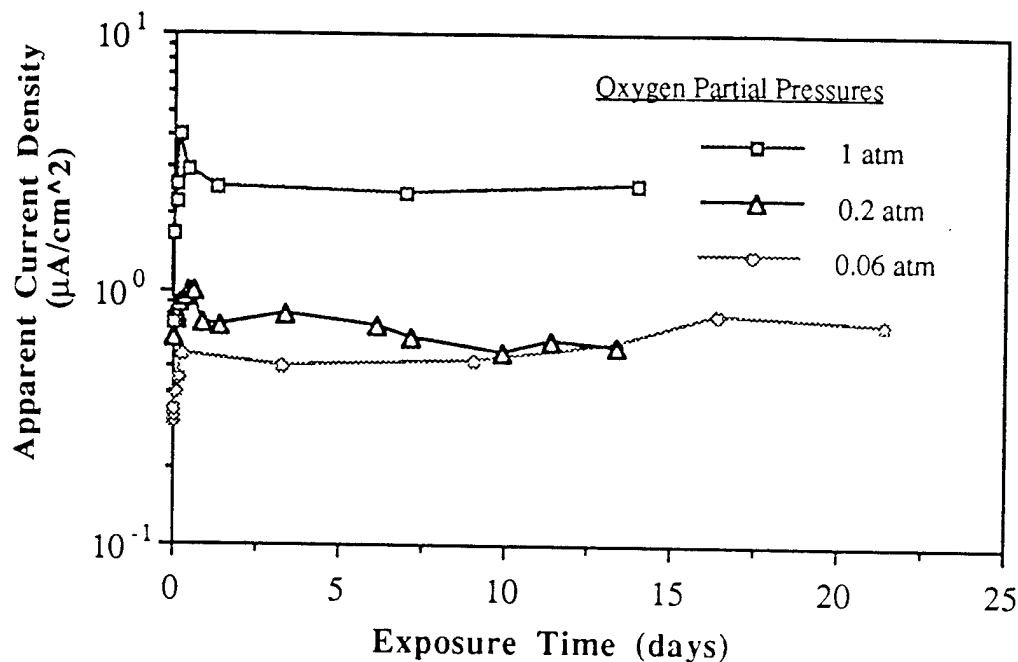
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Figure 4. Current time profiles for three oxygen partial pressures at -900 mV(SCE) for a carbon fiber vinyl ester composite.

This indicates that the carbon fibers in the carbon fiber vinyl ester composite support oxygen reduction reaction producing hydroxyl ions under the applied potential conditions. Moreover, the variation of corrosion current with oxygen concentration is direct evidence that the current is diffusion limited by oxygen diffusion rates towards the cathode. The existence of diffusion limited current in carbon/vinyl ester composites was earlier reported[2] and is shown in figure (5).

The plot in figure (5) shows a comparison of potential-current density plots between a carbon fiber composite and free carbon fibers. It can be easily seen that the current is diffusion limited for both cases. The fact that increased debonded area results at higher oxygen concentrations coupled with the fact that the current density is proportional to oxygen concentration implies that the significant current is liberated only at these damaged areas of the composite and the current at the carbon/polymer interface is negligible. The steady state current value for the low oxygen case is same as that of the medium oxygen case. One possible reason for this behavior is as follows: The faces of the sample other than the exposed face to electrolyte were exposed to the ambient. Therefore, even though the electrolyte contains less oxygen for the low oxygen case, oxygen from the atmosphere (partial pressure = 0.2

atm) permeates through the sides of the sample, into the sample, resulting in a higher steady state current density.
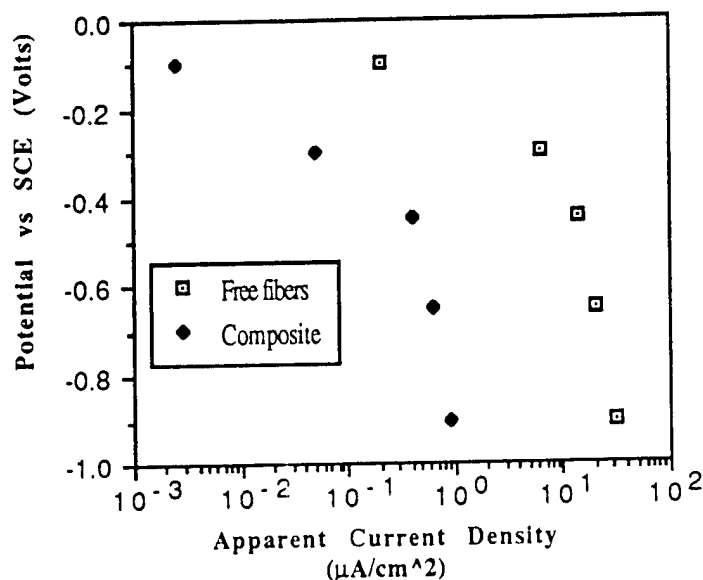

Figure 5. Potential current density data for free carbon fibers and for a carbon fiber vinyl ester composite.

The composite samples, before exposure, were all in equilibrium with atmosphere and therefore were saturated with air from the atmosphere. The higher current above the steady state values for the medium and high oxygen concentrations is due to the high oxygen concentration inside the composite at the initial condition. Once this happens, the near fiber region will be devoid of oxygen and the current drops to a steady value determined by the amount of oxygen in solution. However, the high initial current greater than the steady state value is absent for the low oxygen case because of the negligible contribution of oxygen from the electrolyte solution.

The blister detectability time as a function of oxygen partial pressures is shown in Figure (6). It can be seen that 1/BDT, which is proportional to the blister growth rate, increases with increasing oxygen concentration. This indicates that indeed the blistering phenomenon is related to the oxygen reduction reaction and the data serves as a validation of the proposed blistering mechanism.

Since the amount of cathodic debonding is a function of charge liberated or the amount of hydroxyl ions produced at the cathode less the amount diffused away from cathodic sites, it is of interest to determine if the oxygen partial pressures affect the cumulative charge densities. The cumulative charge density (CCD) was calculated by numerically integrating the current densities with respect to time.
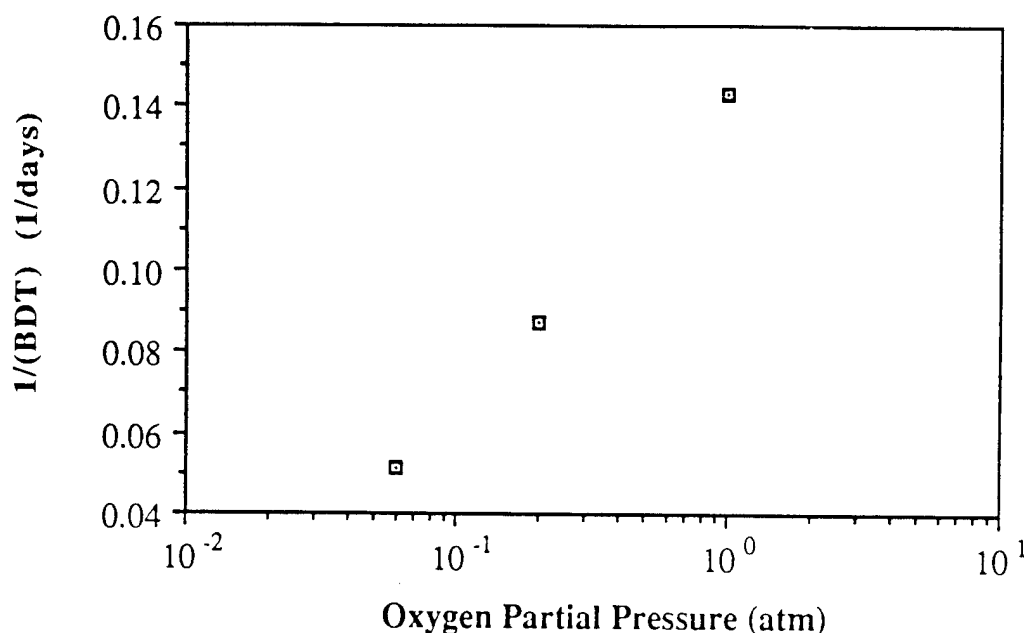
Figure 6. The effect of oxygen partial pressure on galvanic blister growth rate at an applied potential of -900mV(SCE).

The CCD as a function of time for the three cases of oxygen concentrations is shown in figure (7). It can be seen that the charge densities exponentially increase with time initially but at very slow rates at large exposure times.

The most interesting feature is that the cumulative charge densities increase by 4 orders of magnitude during the initial periods of exposure and at the blister detectability time, they all are within the order of magnitude of 1 coulombs per sq. cm. for this composite under the given experimental conditions. The rapid increase of CCD during the initial times was attributed to the combined effect of the increased area of exposure of carbon fibers to the diffusing electrolyte solution and to rupture of small blisters formed on the fibers closest to the surface that expose the fibers and to the change in polymer resistance as water and ions build up inside.

Because the blistering rates are greater for higher oxygen partial pressures, the electrochemical changes were rapid with increasing oxygen concentrations and therefore it would be interesting to compare the impedance behavior in all the three cases at the same normalized exposure time based on the blister detectability time. This comparison at 1% of the BDT for the three cases of oxygen concentration is shown in Figures (8a) and (8b). The Bode plots in these figures show somewhat similar profiles for all the samples.
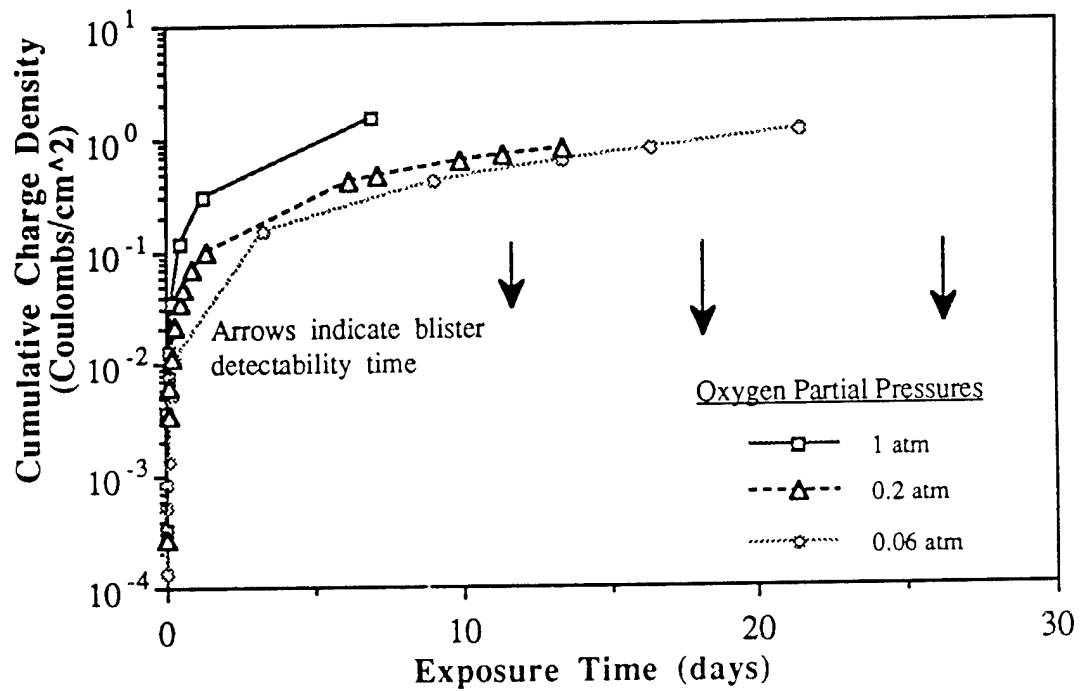
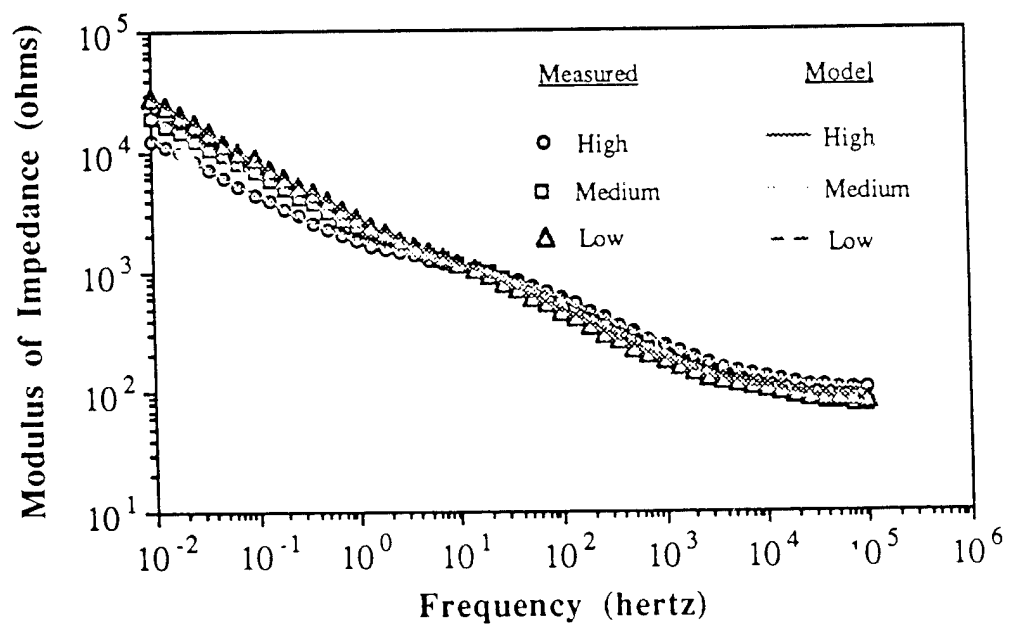Figure 7. Temporal changes in cumulative charge density for blister detection.

Figure 8a. Bode magnitude data and model fit for high (1atm),

medium(0.2 atm) and low (0.06 atm) oxygen partial pressures at -900mV at 1% of blister detectability time.

The Bode phase angle plot shows that the phase angle maxima at lower frequencies shift to lower frequencies and the maxima at the higher frequencies shift to higher frequencies with increasing oxygen concentrations. This indicates that the two time constants differ more with increasing oxygen concentration because of greater reaction rates and increased debonded area for higher oxygen concentrations.
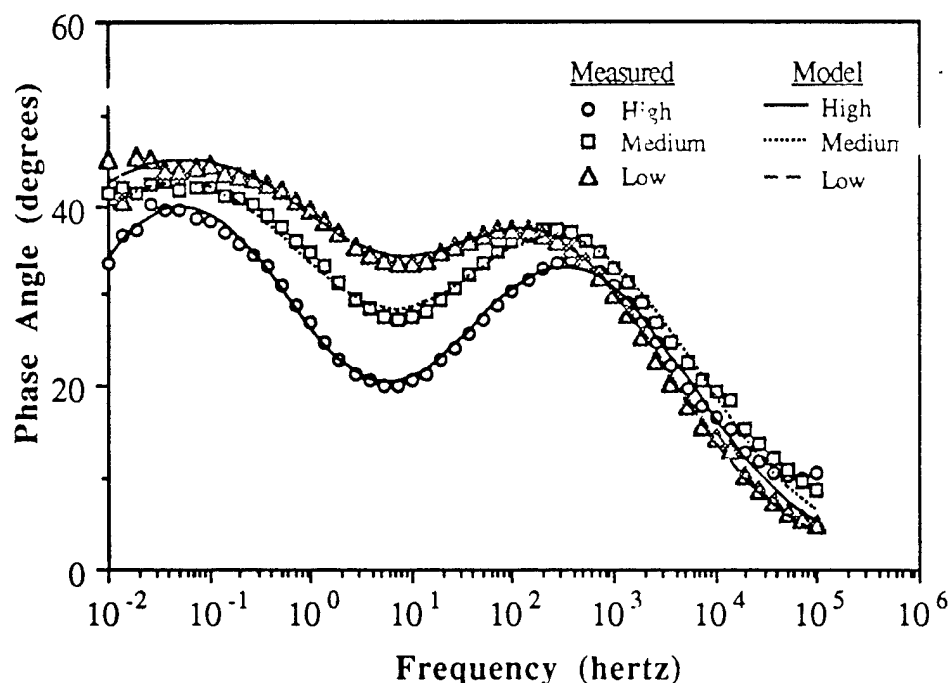

Figure 8b. Bode phase angle data and model fit for the same conditions as figure 8a.

Indeed, the existence of two time constants or two peaks in phase angle dispersion indicates defects in polymer layer where the fibers are directly exposed to the electrolyte. In an earlier investigation it was also proved that the shift of higher phase angle maxima to higher frequencies indicate greater area of exposed fibers to the electrolyte[7]. Therefore, it follows that higher oxygen concentrations in greater damage in the polymer layer due to greater number of blisters.

CONCLUSION

The effects of oxygen concentration on galvanic blistering in carbon fiber composites was investigated and a mechanism for blistering

CONCLUSIONS

1. The fiber type did not significantly influence the degradation mechanisms of the composites under galvanic exposure conditions. The polymer conditions, fiber surface treatment and interface behavior between fibers and polymer matrix are the more important control parameters.

2. The parameters from modeling provided an important degradation mechanisms of composites.

3. The decreasing in polymer resistance, Rp, with increasing time of exposure indicated that dynamic degradation processes were occurring due to the cathodic reaction at the fiber surface. The value of Rp also decreased with increasingly negative applied potentials.

4. The observed damage on exposed specimen provided an evidence of decreasing of impedance behavior of composites.

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